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Effect of aging on chemical and rheological properties of SBS modified asphalt with different compositions

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HIGHLIGHTS

- Components distribution of SBS modified asphalt binder is presented.
- Master curve of the complex modulus (|G*|) and phase angle (δ) of SBS modified asphalt are depicted.
- Phase angle (δ) is more sensitive to asphalt composition and aging.
- Compared to complex modulus, the master curve of phase angle (δ) has more characteristics.

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ABSTRACT

The simultaneous polymer degradation and asphalt oxidation of polymer modified asphalt (PMA) binder make it difficult to understand the rheological behavior of PMA in the aging process. The present study was meant to investigate the rheological behavior of various PMAs before and after aging (Rolling Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV)) by using rheological master curves in combination with Gel Permeation Chromatography (GPC). The GPC test was performed to obtain the average molecular weight (Mw) of the polymer and distribution of asphaltenes and maltenes.

The properties of chemical and rheological were analyzed comprehensively and the results indicated that the phase angle (δ) is more sensitive to asphalt composition (sulfur contents, polymer and base binder characteristic) than the complex shear modulus. Besides, the δ shape can strongly reflect the differences between the rheological responses of the modified asphalts under the different aging conditions. A plateau would occur if the SBS network was formed. Thus the δ shape of SBS modified asphalt will be closer to that of base binder when SBS structure was completely destroyed. Although the degradation of polymer became severer when sulfur was added, sulfur can promote the formation of three-dimensional structures of styrene–butadiene–styrene (SBS) and improve the rheological property of aged PMAs.

1. Introduction

Aging of asphalt is induced by chemical and/or physical changes that occur during the production of pavement and throughout its service life. This causes asphalt to become brittle and has a higher susceptibility to surface cracking, thus reducing the overall service life and riding quality of the asphalt pavements. The principal cause of asphalt aging and embrittlement is the atmospheric oxidation of certain molecules within the formation of highly polar and strongly interacting functional groups containing oxygen [1]. Aging is a highly complex process in neat asphalt binder and complexity increases when polymer-modified asphalt (PMA) is involved.

Due to its excellent engineering property and relatively low cost, styrene–butadiene–styrene (SBS) has been widely applied in the modification of asphalt [2–5]. When SBS is blended with asphalt, the elastomeric phase of the SBS copolymer absorbs the maltenes (oil fractions) from the asphalt and swells up [6,7] finally forming two parts: the asphalt phase and the SBS phase. Thus, the rheological changes in aged SBS modified asphalt are dependent on a combined effect of asphalt oxidation and polymer degradation [8–11]. When assessing the quality of a chosen polymer-modified asphalt through aging properties, both chemical and rheological methods are required.

There has been a lot of research conducted on SBS aging. Lu and Isacsson concluded that aging resulted in the degradation of the

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SBS polymer (a decrease in the polymer molecular weight) and the oxidation of the asphalt (an increase in the content of polar oxygen containing molecules and an increase in asphalt molecular weight) [10]. Oxidative aging decreased the susceptibility of the asphalt to temperature, damaged the polymer network in binders, further broadened the relaxation spectrum, and diminished polymer effectiveness in improving asphalt ductility [12]. SBS modified binders were investigated by Fourier transform infrared (FTIR), atomic force microscopy (AFM), and dynamic shear rheometer (DSR) to observe the changes in morphology and chemical structure [13,14]. Liu and Nielsen investigated the aging properties of SBS modified asphalt from the laboratory to the field by DSR and Gel Permeation Chromatography (GPC) [15].

The results of the investigation indicate that the degree of SBS modification is a function of asphalt source, asphalt–polymer compatibility and polymer concentration [16–18]. Obviously, the chemical and rheological properties of aged PMAs are also affected by these factors. However, the comparison of chemical and rheological properties among different compositions of aged SBS modified asphalt is seldom studied.

In order to analyze the influence of different factors on the chemical and rheological properties of the SBS modified asphalt after aging, a number of SBS modified asphalts were produced with two base binders (ESSO70 and JINSHAN70), two types of polymers (radial SBS and linear SBS), and different sulfur contents (0, 0.15, and 0.25). Aging was assessed via conventional aging tests, such as the Rolling Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV). RTFOT and PAV are expected to simulate, respectively, short-term aging during mixing and long-term aging in the field [19]. The molecular weight distribution, weight average molecular weight ($\overline{M}w$) of the component, the master curve of complex modulus ($|G^*|$), and phase angle (δ) of SBS polymer modified asphalt were observed by means of Gel Permeation Chromatography (GPC) and Dynamic Shear Rheological (DSR), respectively. The relationship between the chemical and rheological properties of different formulation asphalts and the performance ranking of aged PMAs were also analyzed.

2. Materials and methods

2.1. Materials and preparation of SBS modified asphalt binder

In this study, two base binder, two SBS modifier, and elemental sulfur were selected to prepare modified binders in laboratory. Base binder was ESSO asphalt and JINSHAN asphalt. SBS 791-H was produced by Sinopec and SBS T161B was produced by DuShanZi Petroleum and Chemical Corporation, China. SBS 791-H is a kind of linear polymer with an average molecule weight of 110,000 g/mol, containing 30 wt% of styrene. SBS T161B is a kind of radial polymer with an average molecule weight of 230,000 g/mol, containing 30 wt% of styrene. The amount of elemental sulfur ranges from 0% to 0.25% by weight of the base binder (see Table 1).

Preparation of modified binders was divided into three stages. Firstly, SBS was added to base binder and sheared for 30 min at 180 °C with high shear mixer. Secondly, the blend was stirred for 60 min using the mechanical blender. Thirdly, a cross-linking agent (Sulfur Table 2) was added to the blend and stirred for another 90 min.

Table 1
Simplified name and PG grade result.

Base Binder	SBS type	SBS%	Sulfur%	Sample ID	PG	Viscosity@135 °C
ESSO	–	0	0	E70	63.3-23.6	0.493
	linear	4.5	0.15	E4.5L0.15w	73.3-25.4	2.383
	radial	4.5	0	E4.5R0w	72.4-22.0	1.34
			0.15	E4.5R0.15w	74.7-25.9	2.937
			0.25	E4.5R0.25w	75.4-25.4	3.883
JINSHAN	–	0	0	J70	62.8-25.3	0.645
	radial	4.5	0.15	J4.5R0.15w	75.2-26.1	6.358

Note: "−V", "−R", and "−P" stand for: virgin, RTFOT and PAV, respectively.

Table 2
The grain size of the sulfur.

Grain size	>150 μm	75 μm–150 μm
Mass percentage (%)	0	0.4

2.2. Gel permeation chromatography (GPC) test

About 20 mg binder sample was dissolved in tetrahydrofuran (THF) in a 10 mL volumetric flask for 24 h before GPC test. The solution was then filtered through a weighted 0.45 μm PTFE filter and was collected in a 0.5 mL centrifugal tubes for GPC test. Waters 1515 High-Pressure Liquid Chromatography (HPLC) Pump and Waters 2414 Refractive Index (RI) detector were used to perform GPC test THF (HPLC grade) was selected as mobile phase solvents. A combination of three columns was used for separating constituents of asphalt binder by molecular size. The calibration curve was built with Shodex® Polystyrene Standards in order to convert the retention time to molecular weight. A 100 μmL syringes was used to take the sample from the prepared solution in the centrifugal tube as mentioned in the solubility test. After removing the bubble in the syringe, the solution was then injected into the manual sample injector and the solution passed through the columns for 40 min at a flow rate of 1 mL/min. The original data was exported and normalized for further analysis (e.g. Fig. 1). The chromatogram was divided into three slices based on the molecular weight of eluting species. The three fractions are polymers (molecular weight >19,000), asphaltenes (molecular weight from 19,000 to 3000) and maltenes (molecular weight less than 3000) [20]. The contents of asphaltenes and maltenes were calculated accordingly based on Eqs. (1) and (2).

$$Asphaltenes\% = \frac{Area_{asphaltenes}}{Total\,area\,under\,chromatogram} \times 100\% \quad (1)$$

$$Maltenes\% = \frac{Area_{maltenes}}{Total\,area\,under\,chromatogram} \times 100\% \quad (2)$$

The average molecular weight of polymer in the PMA is calculated as follows:

$$\overline{M_w}(polymer) = \sum_{i=1}^{n} \frac{w_i \times M_i}{w_i} \quad (3)$$

$$\overline{M_n}(polymer) = \sum_{i=1}^{n} \frac{N_i \times M_i}{N_i} \quad (4)$$

where $\overline{M_w}(polymer)$ is the average molecular weight; w_i is the weight of molecular mass M_i and is proportional to the RI response; $\overline{M_n}(polymer)$ is the number average molecular weight; N_i is the number of molecules of molecular mass M_i. The calculation of the average molecular weight of the polymer was performed on Origin software. Two replicates were used for GPC test and the average values were reported.

2.3. Frequency sweep test and construction of master curve

A DSR was used to perform frequency sweeps between 0.1 and 30 Hz at temperatures between 5 and 75 °C. The 8 mm diameter, 2 mm gap, parallel plate testing geometry was used for the tests between 5 and 25 °C and the 25 mm diameter, 1 mm gap was used at the temperature range of 35 to 75 °C. The strain amplitude for the frequency sweep tests was within the linear viscoelastic (LVE) response of the binder. The sigmoidal model is developed in National Cooperative Highway Research Program (NCHRP) Project A-37A was taken to construct complex modulus master curve [21]. The reference temperature of 25 °C was chosen for the production of complex modulus and phase angle master curve [16].The sigmoidal model is as follows:

$$\log|G^*| = \nu + \frac{\alpha}{1 + e^{(\beta+\gamma\log f_r)}} \quad (5)$$

where log fr is log reduced frequency; ν is the lower asymptote; α is the difference between the values of the upper and lower asymptote; β and γ define the shape between the asymptotes[21].